USE OF THE MICRODIFFRACTION (M-XRD) TECHNIQUE IN STUDYING PIGMENTS IN ITEMS OF CULTURAL HERITAGE

M.P. Gómez-Tena, E. Zumaquero, C. Machí

Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE). Universitat Jaume I. Castellón. Spain.

pilar.gomez@itc.uji.es

1. INTRODUCTION

The study of materials of historical, artistic, and cultural heritage interest is becoming a growing research line, not only in the field of conservation and restoration, but also in archaeology in general as a way of obtaining information on production processes, commerce, or migration in antiquity.

To date, the destructive character of many analytical techniques has restricted heritage studies, since heritage conservation has been prioritised above and beyond any information that might be obtained. However, the continuous improvements in scientific instruments have made it possible to study these materials in a non-destructive way, without any degradation or alteration in their appearance. X-ray microdiffraction enables a thorough study to be performed of the mineralogy of items of artistic and cultural heritage [1].

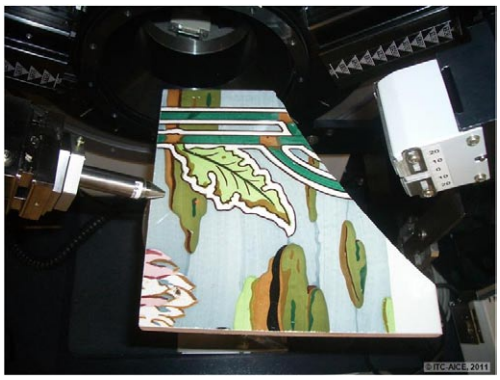
2. OBJECTIVE AND MOTIVATIONS

The main objective of this study was the mineralogical characterisation of the pigments used in the fabrication of earthenware tiles dating from the 14th to the 20th century in the Valencia Region, using X-ray microdiffraction (μ-XRD), which is a non-destructive technique. The technique allows a mineralogical study to be made of the surface of items of cultural heritage value, using a collimated X-ray beam that impinges upon a very small area of the sample, thus analysing rough surfaces, flaws, and even small details that cannot be analysed using the conventional X-ray diffraction technique [2].

The development of this method pursues the creation of new test methodologies in which a parallel X-ray beam and a high sensitivity solid-state detector are incorporated, in order thus to obtain structural information on very small-sized samples.

3. METHODOLOGY AND MATERIALS

The analysis was carried out with a Bruker Theta-Theta model D8 Advance X-ray diffractometer, with Bragg-Bentano geometry and Göbel mirror, primary-beam collimator, a laser that focused the diffraction beam on the point of the surface to be analysed, and a high-resolution solid-state detector (Vantec). The analyses were performed with a copper source, intensity of 40kV–40mA, slit of 0.5º, time constant of 5 seconds, and step size of 0.06º.



4. RESULTS AND DISCUSSION

A small area of the surface of five earthenware tiles with different shades of green, dating from the 14th to the 20th century, was selected to study the pigments that each contained using microdiffraction analysis.

The evaluation of the results indicated that the different shades of green were fundamentally due to the presence of crystalline phases with Co-Zn-Cr spinel structures, a Pb-Fe-Sn-O pyrochlore-type structure, or a Ca-Cr-Si-O garnet structure. Together with these phases, the surface of the tiles was also found to contain opacifying agents such as tin oxide and quartz. The absence of any chromophore structures in some of the studied tiles was also observed, indicating that the green shade was due to the presence of dissolved copper in the glassy matrix [3].

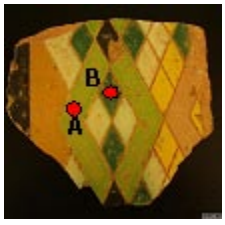
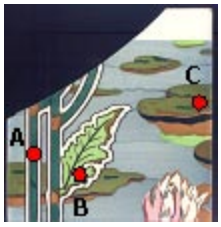
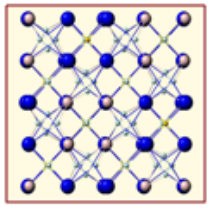
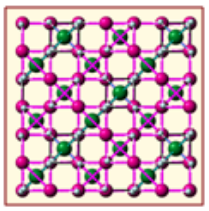
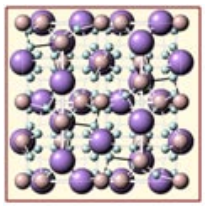
A1 (s XIV)	A2 (s XIX)	A3 (s. XIX)	A4 (s. XIX)	A5 (s. XX)
				
Cassiterite	**Cassiterite** **Pyrochlore group** **Quartz**	**Cassiterite** **Pyrochlore group** **Quartz**	**<u>Area A</u>** **Cassiterite** **Pyrochlore group** **<u>Area B</u>** **Cassiterite** **Quartz**	**<u>Area A</u>** **Cassiterite** **Spinel** **<u>Area B</u>** **Cassiterite** **Pyrochlore group** **Uvarovite** **Quartz** **<u>Area C</u>** **Cassiterite** **Pyrochlore group**
				
Pyrochlore structure	*Spinel structure*	*Garnet structure*		

Table 1. Crystalline phases identified in the analysed earthenware tiles and measured areas

Cassiterite = SnO_2; Pyrochlore group = $Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$; Quartz = SiO_2; Spinel = $(Co,Zn)Cr_2O_4$; Uvarovite (garnet) = $Ca_3Cr_2(SiO_4)_3$

5. CONCLUSIONS

The microdiffraction technique allows items with small and large sizes, and with curved shapes and irregular surfaces to be analysed by measuring very small areas with high sensitivity.

Using the proposed methodology, a non-destructive mineralogical study was conducted of ceramic pigments in Valencian heritage tiles. The information obtained has been useful in studies on dating and restoring the artistic heritage.

The following structures, corresponding to green shades, were determined: Pyrochlore group = $Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$; Spinel = $(Co,Zn)Cr_2O_4$; and Uvarovite (garnet) = $Ca_3Cr_2(SiO_4)_3$.

ACKNOWLEDGEMENTS

The present study was supported by the European Union through the European Regional Development Fund (ERDF) and by IMPIVA (Generalitat Valenciana). (IMIDIC/2009/2 –IMIDIC/2010/75).

REFERENCES

[1] VIZCAINO MARTÍ, M.E. Cerámica barroca en Valencia, Valencia: Ayuntamiento de Valencia, 1998.

[2] DOMÉNECH CARBÓ, M.T.; YUSÁ MARCO, D.J. Aproximación al análisis instrumental de pigmentos procedentes de obras de arte. Valencia: UPV, 2006.

[3] HACKENS, T.; SCHVOERER, M. Datation-caractérisation des céramiques anciennes: cours intensif européen. Paris: CNRS, 1984.